Indian J. Phys. 49, 615-622 (1975)

On the electrical resistivity of noble metals

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(*Received* 28 *April* 1975)

The modified deLaunay lattice dynamical model is used to study the temperature variation of electrical resistivity of noble metals within free electron approximation. Bardeen matrix elements for the scattering of free electrons have been incorporated into the variational expression of the Boltzmann transport equation. The distinction between the Normal process and Umklapp process has been affected in a realistic manner. The computed temperature dependence of electrical resistivity of copper, silver and gold has been compared with the corresponding experimental data and the agreement is found to be satisfactory

1. INTRODUCTION

One of the aims of the solid state theory is to give a proper account of the transport properties of monovalent metals. It was Bloch (1928) who first initiated the investigation and qualitatively accounted for the electrical resistivity of metals. Bardeen's (1937) classical calculations convincingly demonstrated the validity of Bloch-Wilson theory of electrical resistivity of metals which is a landmark in the study of transport properties. The complete phonon spectrum on the basis of Born von Karman lattice dynamical model was taken into account by Bailyn (1958) in the electrical resistivity calculations of alkali metals. With the availability of band structure calculations, the study of transport properties of metals gained momentum. Bross *et al* (1963) and Hasegawa (1964) accounted for the electronic band structure and the anisotropy of the lattice spectrum in the electrical resistivity calculations for alkali metals. Baym (1964) developed an algorithm to calculate the electrical resistivity with the help of experimentally determined dynamical structure factor. This method in turn was successful in incorporating multiphonon and Umklapp processes in the electron-lattice interaction without having to use a phonon description of the lattice oscillations. However due to inadequate knowledge of structure factor Baym (1964) could not perform the numerical calculations. Greene *et al* (1965) have studied the electrical resistivity of sodium. Their calculations incorporate the many body effects, the Umklapp process, time dependent effect and the dynamics of ions from the neutron scattering data but still the agreement with the experimental

results is not satisfactory. Robinson & Dow (1968) have made a very interesting attempt to calculate the transport properties of alkali metals from pseudopotential considerations. They have taken the dynamics of ions from a phenomenological theory and the electron-ion interaction from the Animalu-Heine-Abarenkov pseudopotential. These calculations have taken anisotropy into account but the agreement with the experimental data is not good. Dynes & Carbotte (1968) have extended the procedure of Baym (1964) by using the dynamics of ion from the neutron scattering data. Their results are in good agreement with the experiments. Further modifications have been done by Hayman & Carbotte (1971) by introducing the effect of volume changes through the thermal expansion and they have obtained good agreement with the experimental electrical resistivity of alkali metals over a wide range of temperatures. Recently Rice & Sham (1970, 1971) have used a different pseudopotential in order to calculate the low temperature resistivity of potassium and have separated the total resistivity into Normal and Umklapp components. They have obtained the resistivity expression from the variational solution of the Boltzmann transport equation (Kohler 1948, 1949) with the standard trial function. The calculations of Kaveh & Wiser (1971) on low temperature resistivity of potassium are based on the weak coupling theory for electron phonon interaction and the Boltzmann transport theory.

Goel (1973) has proposed a model for the lattice dynamics of fcc metals which employs a modified form of electron gas model of deLaunay with angular forces. His results for copper are in excellent agreement with the experimental phonon dispersion curves. The model has been successfully applied to the calculations of dispersion curves and Debye-Waller factors of silver and gold by Goel & Sneh (1974). In view of the relative success of the model of Goel (1973) it was thought desirable to employ it to study the temperature dependence of electrical resistivity of noble metals.

The calculations of temperature variation of electrical resistivity of copper, silver and gold within the free electron approximation using the lattice dynamical model of Goel are presented in this paper.

2. Theory

Kohler (1948, 1949) and Sondheimer (1950) have obtained the variational solution of Boltzman transport equation. The variational expression for the electrical resistivity of a cubic lattice is given by (Ziman 1960)

$$\rho = \frac{(1/k_B T) \int\int\int (\phi_k - \phi_{k'})^2 P(kq, k') dk\, dk' dq,}{\left| e \int v_k \phi_k \frac{\partial f_k^0}{\partial E_k} dk \right|^2}, \qquad \ldots (1)$$

In the above expression k_B is the Boltzmann constant, e is the electronic charge, k and k' are the wave vectors of the initial and the final states of electrons, $P(kq, k')$ is the probability of transition of an electron in a k state to a k' state with absorption of phonon wave vector q, v_k and E_k are the velocity and energy of the perturbed distribution of the form

$$f_k = f_k^0 - \phi_k \frac{\partial f_k^0}{\partial E_k}, \qquad \ldots (2)$$

where $f_k^0 = (\exp((E_k - E_F)/k_BT)+1)^{-1}$ is the Fermi function representing the probability of occupany at equilibrium.

Let us assume a trial function $\phi_k = k\,u$, where u is a unit vector in the direction of applied electric field. The trial function leads to the first order variational solution of Boltzmann equation given by

$$\rho = \frac{3\pi\hbar}{2k_Bk_F^2e^2MNTS_F^2} \sum_p \int\int \frac{K^2(K.e_{qp})^2C^2(K)dS_F dS'_F}{[1-\exp(-\hbar\omega_{qp}/k_BT)][\exp(\hbar\omega_{qp}/k_BT)-1]v\,v'}, \qquad \ldots (3)$$

where k_F is the Fermi wave number, M the mass of the atom, N the number of atoms per unit volume, T the absolute temperature, S_F the area of the Fermi surface, ω_{qp} and e_{qp} are the angular frequency and polarization vector of phonon wave vector q and mode of vibration p, v and v' are the velocities of electrons in k and k' states respectively and $K = k' - k$ is the scattering vector. $C(K)$ is the Bardeen matrix element for scattering of free electrons given by

$$C(K) = \frac{[V(r)-E]K^2 - W(K)q_s^2}{q_s^2+K^2}\, G(qr),$$

$[E - V(r)]$ is the kinetic energy of an electron in lowest state at the surface of atomic polyhedra of radius r and $q_s^2 = \frac{4\pi ne^2}{W(K)}$, where n is the electron density with

$$W(K) = \frac{2}{3}E_F\left[\frac{1}{2} + \frac{4k_F^2-K^2}{8k_FK}\ln\left|\frac{2k_F+K}{2k_F-K}\right|\right]^{-1}.$$

The Bardeen interference factor $G(x) = 3(\sin x - x\cos x)/x^3$.

The dependance of ω_{pq} and $(K.e_{qp})$ on the scattering vector K makes the evaluation of the surface integral in eq. (3) difficult. Therefore, we have used the averaging method of Bailyn (1960) to evaluate the double averages. The right hand side of eq. (3) can be written as

$$<< A(K) >> = \frac{1}{S_F^2}\int\int A(K)dS_F dS_F', \qquad \ldots (4)$$

where

$$A(K) = \sum_p \frac{K^2(K.e_{qp})^2 C^2(K)}{[\exp(\hbar\omega_{qp}/k_BT)-1][1-\exp(-\hbar\omega_{qp}/k_BT)]}.$$

In order to effect the average, all the wave vectors k and k' that have the same scattering vector K are considered and an average over such vectors is taken. The obvious advantage of a such preliminary average for a given value of K is that the phonon parameters do not change. Next an average over all K for a given K-magnitude, i.e., $S(K)/\int S(K)d\Omega$ is taken. $S(K) = \pi(4k_F^2 - K^2)^{\frac{1}{2}}$. Finally an average of all such K-magnitudes is taken which is equal to one integral over all K with weight factor equal to $\int d\Omega S(K)/(\int dK \int d\Omega S(K))$. This average over the Fermi surface can be written as

$$<< A(K) >> = \frac{\int d\Omega \int dK A(K)S(K)}{\int d\Omega \int dK S(K)} \quad \ldots (5)$$

We assume the Fermi surface to be perfectly spherical which gives

$$\int d\Omega \int dK S(K) = 4\pi^3 k_F^3. \quad \ldots (6)$$

Therefore, eq. (2) becomes

$$<< A(K) >> = \frac{1}{2\pi^2 k_F} \int d\Omega \int dK A(K)(1-u^2)^{\frac{1}{2}}, \quad \ldots (7)$$

where $u = K/(2k_F)$.

Finally the expression for the ideal electrical resistivity of metals due to phonon scattering is given by

$$\rho = \frac{3\hbar}{4\pi k_B k_F^3 e^2 v_F^2 M N T} \sum_p \int d\Omega \int \frac{dK\, K^2(1-u^2)^{\frac{1}{2}}(K.e_{qp})^2 C^2(K)}{[\exp(\hbar\omega_{qp}/k_BT)-1][1-\exp(-\hbar\omega_{qp}/k_BT)]}. \quad \ldots (8)$$

3. Numerical Computation

The phonon frequencies ω_{qp} and the polarization vector e_{qp} have been obtained from the solution of secular equation of the lattice dynamical model proposed by Goel (1973). The determination of the phonon frequencies becomes trivial if the numerical values of the force constants are known. The evaluation of the force constants has been made with the help of three elastic constants and five zone boundary experimental frequencies. The experimental frequencies are taken from the inelastic neutron spectroscopic measurements of Svensson *et al* (1967), Brockhouse *et al* (1969) and Lynn *et al* (1973) for copper, silver and gold respectively. The elastic constants are taken from the measurement of Overton

et al (1955) for copper and Neighbours *et al* (1958) for silver and gold. The computed values of force constants are given in table 1. α_1, α_2 and β_1 and β_2 are the central and angular force constants for the first and second neighbours constants

Table 1. Values of force constants for noble metals in units of 10^3 dyn cm^{-2}

Element	α_1	β_1	α_2	β_2	α'_1	β'_1	α'_2	β'_2
Copper	29.231	−0.757	−1.821	0.100	30.892	−3.892	1.753	2.474
Silver	24.110	−1.020	−0 562	−0.560	27.505	−5.985	1.888	−0.201
Gold	33.646	−3.018	−3.000	−1.864	39 482	−4.926	3 620	−3.175

while α'_1, α'_2, and β'_1, β'_2 are the corresponding modified force constants for the longitudinal component of the wave motion.

The electrical resistivity of noble metals have been calculated from eq. (8) by a modified Houston's method for calculations of phonon spectrum. The integration over the solid angle Ω has been performed with the help of the modified Houston's six direction approximation as elaborated by Betts *et al* (1956). The six directions of K used are (100), (110), (111), (210), (211) and (221). The integration over the vector K has been carried out numerically to take into accounts the elastic anisotropy. A distinction between Normal and Umklapp processe has been made while integrating over K. The significant contribution of the Umklapp process to the total resistivity at high temperatures has been known to exist for a long time (Bardeen 1937) but its substantial contribution to the low temperature resistivity has been realised very recently (Bailyn 1958, 1960; Bailyn *et al* 1956 ; Black 1972). Hasegawa (1964) has evaluated the contribution of Umklapp process to the electrical resistivity in alkali metals. Bailyn (1958, 1960) and Hasegawa (1960) have assumed in their investigation the range for $0 \leqslant u \leqslant 0.63$ correspond to Normal process while $0\,63 \leqslant u \leqslant 1$ correspond to Umklapp process where u is the variable of integration. This separation between the two processes seems rather artificial. Black (1972) has studied the contribution of Umklapp process to the total resistivity of alkali metals without accounting for multiphonon processes. Ekin (1971) and Ekin *et al* (1971) have explicitly separated the resistivity into the Normal and Umklapp contributions and have studied the role of Umklapp process in low temperature resistivity of metals. In the present study the distinction between the two processes have been affected in a realistic manner by actually finding out which contributions are Umklapp and which are not (Kumar *et al* 1975). The scattering vector $K = q$, for normal process where the phonon wave vector q is resistricted to lie in the first Brillouin zone. The limiting values of K are obtained from the intersection of the planes of Brillouin zone boundary with the corresponding vectors. In an Umklapp

process $K = q+G$, where G is the reciprocal lattice vector. In an Umklapp process K goes beyond the boundary of the first Brillouin zone but q is restricted to lie within it. The minimum value of K at which the Umklapp process starts contributing to the total resistivity can be obtained from the geometry of the reciprocal lattice for face centered cubic structure.

A computer programme in FORTRAN IV has been written in order to perform these calculated. The developed algorithm has been simulated on IBM 360/44 computer system.

4. Results and Discussion

The low temperature electrical resistivity of copper has been measured by Berman & MacDonald (1952), White (1953) and Moore *et al* (1967). Berman *et al* (1952) have reported their measurement in the temperature range 2–90 K and White (1953) has reported up to 290 K while the measurements of Moore *et al* (1967) are in the temperature range 70–300 K The only measurements on silver are due to White & Woods (1959). Very recently Cook & van der Meer (1970) have measured the electrical resistivity of gold from 70 K to 300 K The results of the calculations of the electrical resistivity of copper, silver and gold are given in figure 1 For comparison, we have also plotted the experimental data obtained at different temperature. It is seen from figure 1(a) that the theoretical curves of electrical resistivity of copper are in good agreement with the experimental data of White (1953). Figures 1(b) and 1(c) show a satisfactory agreement with the experimental data. There is gradual and systematic departure of experimental electrical resistivity from theoretical results. This deviation increases as one goes from silver to gold.

It has been observed that the distinction between the Normal and the Umklapp processes, which has been affected in a manner discussed earlier, has a considerable affect on the numerical value of electrical resistivity. This emphasises the role played by Umklapp contribution in the resistivity calculations. Umklapp contribution to the total resistivity increases systematically with the temperature. Its contribution to the total resistivity at room temperature has been found to be 20, 25, 40 per cent approximately in the case of copper, silver and gold respectively. This gradual increase in the Umklapp contribution can be attributed to the fact that the temperature variation of the resistivity is very sensitive to the details of an anisotropic phonon spectrum which becomes increasingly important as the temperature increases.

The systematic deviation of the theoretical resistivity from the experimental data as one goes from copper to gold, may be attributed to the increasingly distorted Fermi surfaces. The Fermi surface of copper is almost spherical whereas it is somewhat distorted for silver and more so for gold. The distortions in the

Fermi surface enhance the probability of Umklapp scattering of electron wave function on different parts of Fermi surfaces, thereby changing the numerical value of electrical resistivity. The discrepancy between theory and experiments can be attributed to the use of Bardeen model for electron-phonon matrix elements which ignores the exchange and correlation effects. Another source of discrepancy is the neglect of temperature dependence of elastic constants and other anharmonic effects.

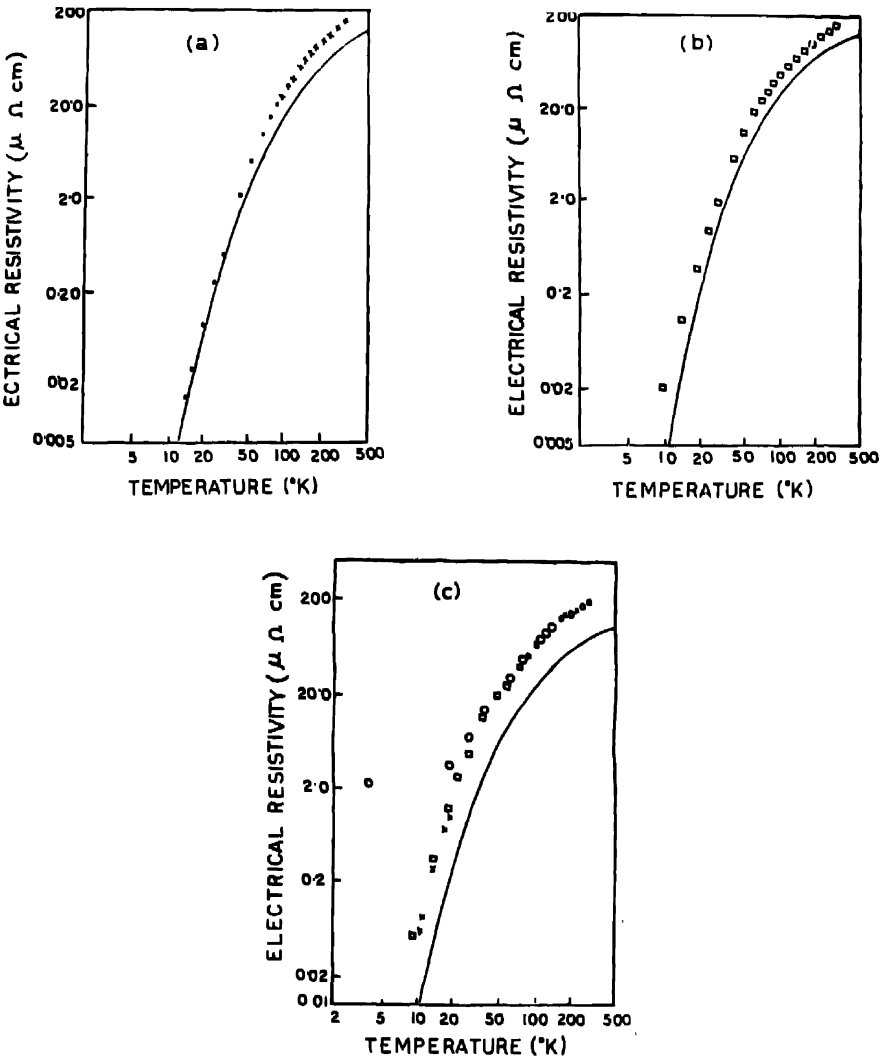

Fig. 1. Variation of electrical resistivity of (a) copper, (b) silver, and (c) gold with temperature. Full curves are theoretical results. Experimental points ● White (1953), × Moore *et al* (1967), □ White *et al* (1959), × Gruneisen (1933) and O Cook *et al* (1970).

However, it is concluded that the present study based on Bardeen model of scattering of free electrons coupled with the lattice dynamical model of Goel provides a satisfactory description of the temperature variation of the electrical resistivity of noble metals.

ACKNOWLEDGMENT

The author is grateful to Miss Sneh Gupta for her help in the numerical computations.

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